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Precise assignment of excited-state bond length using branching ratio measurements: The $B^2\Sigma^+$ state of BaH molecules

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Vibrational branching ratios in the $B^2\Sigma^+ - X^2\Sigma^+$ and $A^2\Pi - X^2\Sigma^+$ optical-cycling transitions of BaH molecules are investigated using spectroscopic measurements and *ab initio* calculations. The experimental values are determined using fluorescence and absorption detection. The observed branching ratios have a very sensitive dependence on the difference in the equilibrium bond length between the excited and ground state, Δr_e : a 1 pm (.5%) displacement can have a 25% effect on the branching ratios but only a 1% effect on the lifetime. The measurements are combined with theoretical calculations to reveal a clear preference for one particular set of published spectroscopic values for the $B^2\Sigma^+$ state ($\Delta r_e^{B-X} = 5.733$ pm), while a larger bond length difference ($\Delta r_e^{B-X} = 6.3-6.7$ pm) would match the branching ratio data even better. By contrast, the observed branching ratio for the $A^2\Pi_{3/2} - X^2\Sigma^+$ transition is in excellent agreement with both the *ab initio* result and the spectroscopically measured bond lengths. This shows that care must be taken when estimating branching ratios for molecular laser cooling candidates, as small errors in bond length measurements can have outsize effects on the suitability for laser cooling. Additionally, our new calculations agree more closely with experimental values of the $B^2\Sigma^+$ state lifetime and spin-rotation constant, and revise the predicted lifetime of the $H^2\Delta$ state to 9.5 μs .

INTRODUCTION

Spectroscopy is one of the most precise measurement tools in physical chemistry. A typical parameter determined using such techniques is r_e , the equilibrium bond length that is often reported with an uncertainty of 1 fm or $< 10^{-5}$, less than the width of an atomic nucleus. By contrast, a bond length calculated using quantum chemistry methods within 1 pm of the experimental value is regarded as very good, especially for excited states, and within 0.1 pm as state of the art except for very small systems. Even BeH, with only five electrons, presents challenges for theory [1]. *Ab initio* quantum chemistry, however, directly calculates values such as r_e that spectroscopic studies only infer via the determination of B_e , the equilibrium rotational constant. Furthermore, B_e itself cannot be directly measured: instead, it is calculated from the measured rotational constants B_v for at least two vibrational levels v . Spectroscopic methods are very reliable when a single isolated potential energy curve is under analysis but become less robust when several potential curves are closely spaced in energy and interact strongly. In such cases a model must be applied to the coupled potentials, and its details influence the derived values of constants such as B_e .

In this work, a combination of branching ratio measurements and calculations is used to distinguish between spectroscopic measurements of r_e that were originally reported to five decimal places but disagree at the second decimal place. Furthermore, we report a new bond length that is consistent with our branching ratio measurements.

The sensitivity of our method relies on monitoring the branching ratios of highly diagonal ($\Delta v = 0$) transitions, where a small change in the decay to additional quantum states results in a large increase in the relative populations of those states. We find that the branching ratios sensitively depend on the difference in the excited- and ground-state equilibrium bond length. An example of a molecule with this property is barium monohydride, BaH, a radical of interest for direct laser cooling [2–4]. For BaH, a 1 pm (.5%) relative bond-length displacement can have a 25% effect on the branching ratios but only a 1% effect on the natural lifetimes. Conversely, this sensitivity implies that care must be taken when theoretically evaluating the laser cooling prospects of new molecular candidates, since branching ratios – key parameters for laser cooling – are strongly affected by small errors in the relative bond length of the electronic states used in the cooling scheme.

BAH SPECTROSCOPY BACKGROUND

The optical and near-infrared spectra of BaH [5–19] are dominated by the three $5d$ -complex states that correlate to the $5d$ state of the Ba atom: $B^2\Sigma^+$, $A^2\Pi$, and $H^2\Delta$. Since all three lie below the ground-state dissociation threshold, the only decay mechanisms are radiative. In addition, these three low-lying excited states possess spectroscopic parameters that closely resemble the $X^2\Sigma^+$ ground state. The resulting diagonal Franck-Condon (FC) factors ensure absorption-emission cycles

numbering in the thousands, as required for efficient laser cooling with as few optical fields as possible. A buffer gas beam [20] of BaH molecules [3] in the $X^2\Sigma^+_{1/2}$ $v'' = 0$, $N'' = 1$ state was recently demonstrated [4] and used in precise measurements of the $(0-0)$ and $(0-1)$ branching ratios, where $(v'-v'')$ denotes an electronic transition between the lower v'' vibrational level and the v' level in the excited state, in the $B^2\Sigma^+ - X^2\Sigma^+$ transition. In addition, the quantum state purity of the buffer gas beam was exploited in measurements of the magnetic g -factors and hyperfine structure of the lowest rovibronic levels of the $A^2\Pi_{1/2}$ and $B^2\Sigma^+_{1/2}$ states [4] in preparation for laser cooling experiments.

One of the potential laser cooling transitions, $B^2\Sigma^+ - X^2\Sigma^+$, is the focus of our study. The $(0-0)$ and $(1-1)$ vibronic bands of BaH were first reported in 1933 [5], and soon extended [7] to include the much weaker off-diagonal bands $(1-0)$ and $(2-1)$. The equivalent study on BaD was published thirty years later [9]. High-quality Fourier-transform data of BaH [11] provided a hundred-fold improvement in the accuracy of the reported spectroscopic constants and extended the analysis to the $B^2\Sigma^+$ $v' = 0-3$ vibronic levels, while the $B^2\Sigma^+$ $v' = 0$, $J = 11/2$ level lifetime [18] was measured to be 124(2) ns.

A more comprehensive analysis [15] attempted a simultaneous fit of spectroscopic data involving all the $5d$ -complex states. A total of 1478 BaH spectral lines and 2101 BaD lines were used in this study. This is currently the only experimental measurement of the spin-orbit splitting in the $H^2\Delta$ state, $A = 217.298 \text{ cm}^{-1}$ for $\nu' = 0$. There is, however, a disagreement between the measured value of the spin-orbit separation in the $A^2\Pi$ state, $A = 341.2 \text{ cm}^{-1}$ for $v = 0$, with an earlier value [9] of 483 cm^{-1} . In addition, the spin-rotation constants for both the $v = 0$ and $v = 1$ levels in the $B^2\Sigma^+_{1/2}$ state are an order of magnitude smaller and of opposite sign to those from previous work [5, 7, 11]. Finally, due to the challenges of working with higher vibrational levels, the spectroscopic constants are limited [13, 15] to the $v = 0$ and $v = 1$ levels for all three $5d$ -states.

Detailed information on higher lying vibrational levels is missing for all the states, as diagonal transitions mean that only a small part of the potential curves can be explored spectroscopically. In the absence of such experimental data, quantum chemistry can be used to explore these dark regions of the potentials [21–23]. *Ab initio* techniques have also been applied to understand the laser cooling process [2, 24, 25]. The latest theoretical study on BaH (Ref. [23], here referred to as Moore18) includes spin-orbit coupling as well as other relativistic effects and a thorough analysis of all the decay pathways. The computed spectroscopic constants for all three $5d$ -complex excited states were in good agreement with experiments. However, in an effort to improve the reliability of the excited state decay properties, the calculated potentials

were shifted to within 0.1 pm of the experimental values for r_e . For the $B^2\Sigma^+$ state the chosen experimental data came from Appelblad *et al* [11]. This study was broadly consistent with earlier spectroscopic measurements [5, 7] but to a greater reported precision. Moreover, it broadened the published potential-energy and rotational constant (T_v and B_v) data to cover the vibrational levels $v = 0-3$, and it quoted B_e (in cm^{-1}) to an accuracy of six decimal places. The experiment dated within two years of the measurements by Bernard *et al* [13, 15] that covered only the vibrational states $v = 0$ and $v = 1$. Oddly, applying this correction reduced the agreement with the measured lifetime [18] of the $B^2\Sigma^+$ state, although the difference was $< 1.5\%$. Also disappointingly, the agreement with the $B^2\Sigma^+_{1/2} - X^2\Sigma^+_{1/2}$ branching ratio measurement [3] became significantly worse.

To shed light on these discrepancies, here we report a new accurate measurement of the branching ratios, using an infrared camera with a cryogenic beam. We combine the measurement with the most detailed *ab initio* work to date to confirm the correct bond length in the excited $B^2\Sigma^+$ state. Adopting a slightly different approach to Moore18 is shown to improve both the spectroscopic constants and the calculated lifetime of the $B^2\Sigma^+$ state. Adjusting the upper-state r_e to match the work of Bernard *et al* [15] does significantly improve the agreement, although the theoretical value still remains outside the error bars of the experimental result. Based on our measurements and quantum chemistry calculations, we suggest a new value of r_e that is based on the very sensitive branching ratio measurements rather than on spectroscopy alone.

FRANCK-CONDON FACTOR RATIO MEASUREMENTS

To perform measurements of the branching ratios for the relevant electronic transitions in BaH, we utilize two complementary techniques, both using our cryogenic BaH molecular beam [4]. The schematic of the experiment is shown in Fig. 1. The BaH beam is generated via ablation of a BaH₂ rock inside a helium-filled copper cell cooled to 6 K. A pair of cell windows allow optical access for a resonant laser beam, which can be used to monitor absorption by measuring the transmitted power on a photodiode (PD). The molecules rapidly thermalize with the helium and are swept out of the cell to form a beam. The cold molecules then travel ~ 40 cm downstream where they enter a detection region equipped with two types of photodetector: a near-infrared-enhanced photomultiplier tube (PMT) and a deep-depletion charge-coupled device (CCD) camera. Each of the two detectors includes dichroic bandpass (BP) filters as shown in Fig. 1, and are used for fluorescence detection.

Both absorption and emission measurements were

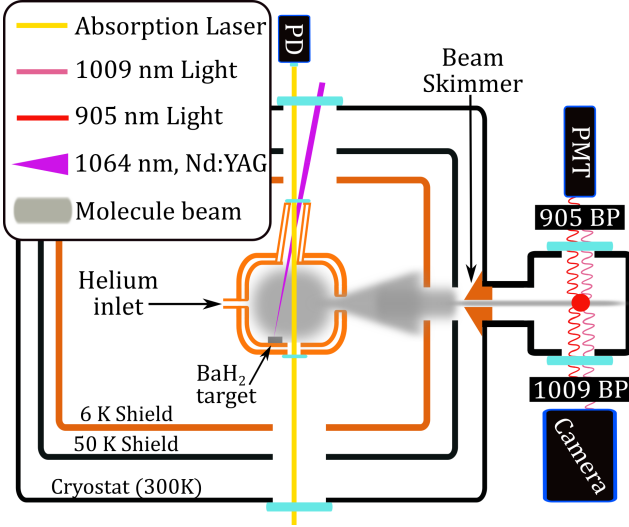


FIG. 1. Diagram of the buffer-gas-cooled molecular beam source used in the experiment. BaH molecules are generated via ablation inside a helium-filled copper cell, then swept through a series of apertures and beam skimmers to form a collimated beam. The beam enters a detection region 40 cm downstream where resonant laser light (905 nm, represented by the red dot, with the beam propagating perpendicular to both the molecular beam and detectors) excites the molecules to the $B^2\Sigma^+ v=0, J=1/2$ level with (+) parity. Two detectors monitor fluorescence to the $X^2\Sigma^+ v=0$ state at 905 nm and to the $X^2\Sigma^+ v=1$ state at 1009 nm. Dichroic bandpass (BP) filters isolate specific decay channels for each detector. The PMT is used to continuously monitor the beam flux.

made on the beam. The absorption technique is based on a differential measurement of the absorption cross section from one ground vibrational state v'' to two different excited vibrational levels v' [26]. We write the integrated absorption cross-section for a rovibronic transition [27, 28] as

$$\begin{aligned} \sigma_{v'J'v''J''}(\tilde{\nu}) &= \frac{g(c\tilde{\nu})(2J'+1)}{8\pi(2J''+1)} \frac{A_{v'J',v''J''}}{(\tilde{\nu}_{v'J'v''J''})^2} \\ &= \frac{2\pi^2\tilde{\nu}_{v'J'v''J''}}{3\epsilon_0 h(2J''+1)} g(c\tilde{\nu}) S_{v'J',v''J''}, \end{aligned}$$

where $\tilde{\nu}_{v'J'v''J''}$ is the transition wavenumber, $A_{v'J',v''J''}$ is the Einstein A-coefficient describing the absorption to the $v'J'$ excited rovibrational state from the $v''J''$ ground level, ϵ_0 is the vacuum permittivity, and $g(c\tilde{\nu})$ is the line-shape function. The transition line strength is

$$S_{v'J',v''J''} = |\langle \Lambda' v' J' \epsilon' | \mu | \Lambda'' v'' J'' \epsilon'' \rangle|^2 = |M|^2 S_{J',J''}, \quad (1)$$

where ϵ is the parity label, $|M|^2$ is the square of the vibronic transition moment, and $S_{J',J''}$ is the Honl-London factor for the transition [29]. As all the transitions studied originate on a level where $J=1/2$, and the principal

results are the ratios between transitions with identical $\Delta J = J' - J''$ values, we drop the explicit references to J . The $|M|^2$ is approximately the product of $q_{v'v''}$, the transition's FC factor, and $|R_e|^2$, the square of the electronic transition dipole moment (all the transitions studied here preserve the electronic spin),

$$|M|^2 = |\langle \Lambda' v' | \mu | \Lambda'' v'' \rangle|^2 \approx q_{v'v''} |R_e|^2.$$

In the results we quote the FC factors $q_{v'v''}$, although we technically measure the vibronic moments.

We relate the cross section $\sigma_{v'v''}(\omega)$ to an experimentally measurable optical absorption to give the absorbance $A(v', v'')$,

$$\frac{\Delta I}{I} = 1 - e^{-N\sigma_{v'v''}(\omega)l} \equiv 1 - e^{-A(v', v'')},$$

where N is the molecular density, ω is the angular frequency of light, and l is the path length. By taking the ratio of absorption between two transitions that differ only in the excited state vibrational number ($v' = 0$ or 1), we can cancel the dependence on every parameter except $q_{v'v''}$ and $\tilde{\nu}$, where the latter is known to a high accuracy. We can then relate the experimentally measured absorption ratio to the ratio of the FC factors for the transitions pairs, or the absorption vibronic transition ratio

$$\text{VTR} = \frac{A(v_1, v'') \tilde{\nu}_{v_2 v''}}{A(v_2 = v'', v'') \tilde{\nu}_{v_1 v''}} \approx \frac{q_{v_1 v''}}{q_{v_2 v''}}. \quad (2)$$

This definition ensures that the quoted VTR is always < 1 for a diagonal system such as the electronic transitions in BaH. Measurements of the VTR using this technique are consequently invariant to potential changes in the molecular density and relies only on quantities we can accurately determine.

The measurement of the emission VTR relies on a direct observation of a decay probability ratio. The ratio $\mathcal{R}_{v'v''}$ of the measured emission to the total overall decay rate (branching ratio) can be expressed in terms of the transition FC factor [30],

$$\mathcal{R}_{v'v''} = \frac{q_{v'v''} \tilde{\nu}_{v'v''}^3}{\sum_{k=0}^{\infty} q_{v',k} \tilde{\nu}_{v',k}^3}, \quad (3)$$

where the summation is over all available radiative decay channels. By observing simultaneous fluorescence from a single excited rovibrational state $v' = 0, J' = 1/2$ to two different vibrational ground states, $v'' = 0$ and 1, we directly compare the relative decays $\mathcal{R}_{0v''}$ and determine the $q_{v'v''}$ ratio for the two transitions,

$$\text{VTR} = \frac{I_{0v_1} \tilde{\nu}_{0v_2}^3}{I_{0v_2} \tilde{\nu}_{0v_1}^3} \approx \frac{q_{0v_1}}{q_{0v_2}}, \quad (4)$$

Electronic transitions	VTR ^a	Experimental value	Theoretical ^b	Proposed
$A^2\Pi_{3/2} \leftarrow X^2\Sigma^+$	q_{10}/q_{00}	0.037(2)	0.037	0.037
$B^2\Sigma^+ \leftarrow X^2\Sigma^+$	q_{10}/q_{00}	0.072(6)	0.059	0.076
$B^2\Sigma^+ \leftarrow X^2\Sigma^+$	q_{01}/q_{11}	0.115(5)	0.072	0.118
$B^2\Sigma^+ \rightarrow X^2\Sigma^+$	q_{01}/q_{00}	0.092(20)	0.045	0.065

^a $J'' = J' = 1/2$ for the absorption lines.

^b Bernard *et al* [15] r_e value used

^c With the proposed +1.5 pm shift in the $B^2\Sigma^+$ bond length

TABLE I. Comparison between the present experimental measurements of the vibronic transition ratios (VTRs) and the corrected theoretical results. $q_{v'v''}$ is the ratio of vibronic transition moments between the v' th level in the excited state and the v'' th level in ground state. The ground state is the Morse-Long range (MLR) potential based on ACVnZ/CBS MLR calculations [22] and the excited states are based on ACVQZ potentials. The difference in equilibrium bond lengths between the excited and ground states, $\Delta(r_e)$, is set at the value proposed by Bernard *et al* [15] for the theoretical values, and the last column corresponds to the longer excited-state bond length proposed here for $B^2\Sigma^+$.

where I_{0v_i} is the intensity of the observed decay to the i th ground vibrational state. These complementary techniques allow us to measure a variety of $q_{v'v''}$ ratios using a series of differential measurements. The experimental results, and the comparison to theoretical work presented below, are provided in Table I. All the ground-state rovibrational levels involved are of $(-)$ parity ($N'' = 1$).

Relative absorption measurements

For absorption measurements we utilize the high molecular density inside the cryogenic cell (Fig. 1). We alternate the probe beam between two coaligned lasers, each tuned to the resonant frequency of the energy levels of interest, with intensities well below saturation. This allows for real-time cancellation of any variability in the molecular yield, as the lasers intersect the same region of the cell. We performed three measurements, obtaining q_{10}/q_{00} for the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ and $A^2\Pi_{3/2} \leftarrow X^2\Sigma^+$ electronic transitions, and q_{01}/q_{11} for $B^2\Sigma^+ \leftarrow X^2\Sigma^+$. To measure q_{01}/q_{11} , an additional laser was coaligned with the absorption lasers and tuned to the $A^2\Pi_{3/2} v = 1 \leftarrow X^2\Sigma^+ v = 0$ transition. This is required to increase the population in the $X^2\Sigma^+ v'' = 1$ state, as the $v'' = 1$ population is negligibly small for BaH thermalized to 6 K [3]. Only the Q_{12} rotational lines (Fig. 3) were measured for each transition. Figure 2 shows a representative measurement including the absorption signals and their ratio. The experimental values for the FC factor ratios thus obtained are presented in Table I (top three entries).

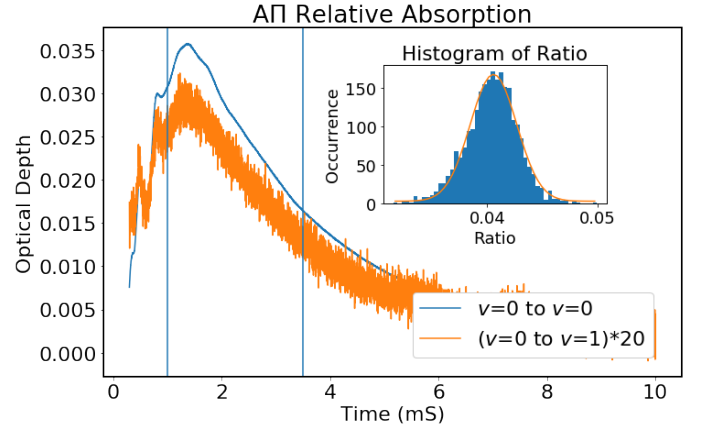


FIG. 2. Relative absorption on the the $A^2\Pi_{3/2} v = 0 \leftarrow X^2\Sigma^+ v = 0$ and $A^2\Pi_{3/2} v = 1 \leftarrow X^2\Sigma^+ v = 0$ electronic transitions, showing the average absorption on each transition over 200 experimental shots. Vertical bars indicate the region of the signal used to calculate the absorption ratio, and error bars for the absorption ratio are conservatively taken as the FWHM of the distribution. This absorption ratio can be related to the FC factor ratio using Eq. (2).

Direct fluorescence detection

To perform a direct measurement of the emission VTR in the decay of the $B^2\Sigma^+ v' = 0$ state, near-infrared fluorescence is recorded from the BaH molecular beam. The measurement is carried out via simultaneous collection of spontaneous emission light as the molecules decay from $B^2\Sigma^+ v' = 0$ to $X^2\Sigma^+ v'' = 0$ at the 905.3 nm wavelength, and to $X^2\Sigma^+ v'' = 1$ at 1009.4 nm. The emission VTR is then related to the FC factor ratio as in Eq. (4).

In the detection region, the molecules are excited to the $B^2\Sigma^+ v' = 0, J = 1/2 (+)$ level using two external-cavity diode lasers (linewidth ≈ 1 MHz) on resonance with the

$$B^2\Sigma^+(v = 0, N = 0, J = 1/2) \leftarrow X^2\Sigma^+(0, 1, 1/2)$$

and

$$B^2\Sigma^+(v = 0, N = 0, J = 1/2) \leftarrow X^2\Sigma^+(0, 1, 3/2)$$

transitions. Prior to the VTR measurement, calibration of the relative efficiency of each collection system is performed by placing a 905 nm BP filter in front of each detector (Fig. 1) and collecting the fluorescence on both. A 1009 nm BP filter was then placed at the CCD camera and simultaneous measurements of fluorescence to the $X^2\Sigma^+ v'' = 0$ and $X^2\Sigma^+ v'' = 1$ states were taken with the PMT and CCD camera, respectively. The ratio of the signals seen on the two detectors and the known efficiency of each filter and detector allow a measurement of the VTR that is independent of the molecule number. Both Q_{12} and P_1 rotational lines (Fig. 3) were measured for each transition as they cannot be distinguished by the filters. The measured value of the q_{01}/q_{00} VTR is

0.092(20). The quoted statistical uncertainty is dominated by shot noise in the calibration and monitor signal due to the relatively poor ($\sim 1\%$) quantum efficiency of the PMT at 905 nm.

THEORETICAL BRANCHING RATIOS

Our theoretical quantum chemistry work concentrates on estimating three observables that present rigorous tests for different aspects of the *ab initio* calculations:

1. $B^2\Sigma^+$ state spin-rotation constants: the spin-orbit and ladder matrix elements;
2. $B^2\Sigma^+$ state lifetimes: transition dipole moments;
3. $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ branching ratios: bond lengths and potential energy functions.

The present experimental study provides the required test for the final property, while previously published work [11, 18] provide the benchmarks for the first two.

Potential energy curves

For initial simulations of the branching ratios, the potentials calculated by Moore18 [23] were used. These *ab initio* calculations of the potential energy curves were performed at a post Hartree-Fock level using a parallel version of the MOLPRO [31, 32] (version 2010.1) suite of quantum chemistry codes. The aug-cc-pCVQZ (ACVQZ) basis set [33] was used on the barium atom to describe the $5s5p6s$ electrons, and the equivalent aug-cc-pVQZ basis for hydrogen [34]. An effective core potential [35] was used to describe the lowest 46 core electrons of the barium atom. The active space at long-range corresponded to the occupied valence orbitals plus the excited $6p5d$ and the lowest Rydberg $7s$ orbital on barium. Once the Hartree-Fock wavefunction had been found, the electron correlation was determined using both the State-Averaged Complete Active Space Self-Consistent Field [36] (SA-CASSCF) and the Multi-reference Configuration Interaction [37] (MRCI) methods for static and dynamic correlation, respectively. Higher levels of correlation were approximated using the Davidson correction [38]. The MRCI wavefunctions were then used to calculate transition dipole moments (TDMs) and spin-orbit coupling matrix elements using the MOLPRO code [39]. Further details on the potentials involved in the present study, namely the ground $X^2\Sigma_{1/2}^+$ and excited $H^2\Delta_{3/2}$, $A^2\Pi_{1/2,3/2}$ and $B^2\Sigma_{1/2}^+$ states shown in Fig. 3(a), can be found in Moore18 [23]. As in Moore18, the traditional Hund's case (a) electronic label is used for those potentials calculated without consideration of spin-orbit coupling such as $B^2\Sigma^+$, while the form $A^2\Pi_{1/2}$ is used

for the final states where Ω , the projection of the total electronic angular momentum on the internuclear axis, is a good quantum number.

To calculate the rovibrational energy levels in each state, the radial Schrödinger equation for each *ab initio* potential is solved using the program DUO [40]. To include the most significant interactions between the states of interest, the treatment includes the electronic states $X^2\Sigma^+$, $H^2\Delta$, $A^2\Pi$, $B^2\Sigma^+$ and $E^2\Pi$ and the relevant spin-orbit matrix elements [39]. The relevant rovibrational levels are shown in Fig. 3(b) for the $B^2\Sigma_{1/2}^+ v=0 \leftarrow X^2\Sigma_{1/2}^+ v=1$ repump transition. While MOLPRO represents all calculations in the C_{2v} point group symmetry, DUO handles $C_{\infty v}$ symmetry states, so appropriate transformations [41] are required to prepare MOLPRO output data for input into DUO as described in Moore18.

Spectroscopic correction to $B^2\Sigma^+$

While the computed rovibrational spacings are in excellent agreement with experiment [23], properties that are particularly sensitive to either r_e or T_e , where T_e is the energy of the potential minimum, may need to be corrected. An example is the spin-rotation structure calculated for each $^2\Sigma_{1/2}^+$ state. The spin-rotation constant γ is predominantly a second-order correction [42] to the energy levels of a $^2\Sigma^+$ state found by summing over $^2\Pi$ states,

$$\gamma = \sum_{n^2\Pi} \frac{\langle BL^+ \rangle \langle \hat{H}_{SO} \rangle}{\Delta E(n^2\Pi - ^2\Sigma^+)}, \quad (5)$$

where $\langle ^2\Sigma^+, 0, -\frac{1}{2} | BL^+ | n^2\Pi, -1, +\frac{1}{2} \rangle \equiv \langle BL^+ \rangle$ are ladder matrix elements, $\langle n^2\Pi, -1, +\frac{1}{2} | \hat{H}_{SO} | ^2\Sigma^+, 0, -\frac{1}{2} \rangle \equiv \langle \hat{H}_{SO} \rangle$ are spin-orbit matrix elements, and $\Delta E(n^2\Pi - ^2\Sigma^+)$ is the energy separation between each $^2\Pi$ state in the summation and the $^2\Sigma^+$ state. Both required matrix elements required are computed using the spin-orbit package within MOLPRO. However, the energy separation between states is crucial, especially when relatively small. For the $B^2\Sigma_{1/2}^+$ state, the largest contributions will be from $A^2\Pi_{1/2}$ and $E^2\Pi_{1/2}$, the former $\sim 1540 \text{ cm}^{-1}$ lower in energy and the latter more than twice this value above the $B^2\Sigma_{1/2}^+$ minimum. As the matrix elements have similar magnitudes (Table 5 in Moore18), the $A^2\Pi_{1/2}$ state has the largest influence on the observed spin-rotation splitting.

The spectroscopic values of T_e and r_e for each electronic state of interest are presented in Table II. The *ab initio* T_e for the $B^2\Sigma_{1/2}^+$ state calculated by Moore18 is in remarkable agreement with the majority of spectroscopic studies and just 120 cm^{-1} higher than the relative outlier by Bernard *et al.* The situation is different for the $A^2\Pi_{1/2}$ state, firstly as there are larger discrepancies between the spectroscopic values, and secondly since the

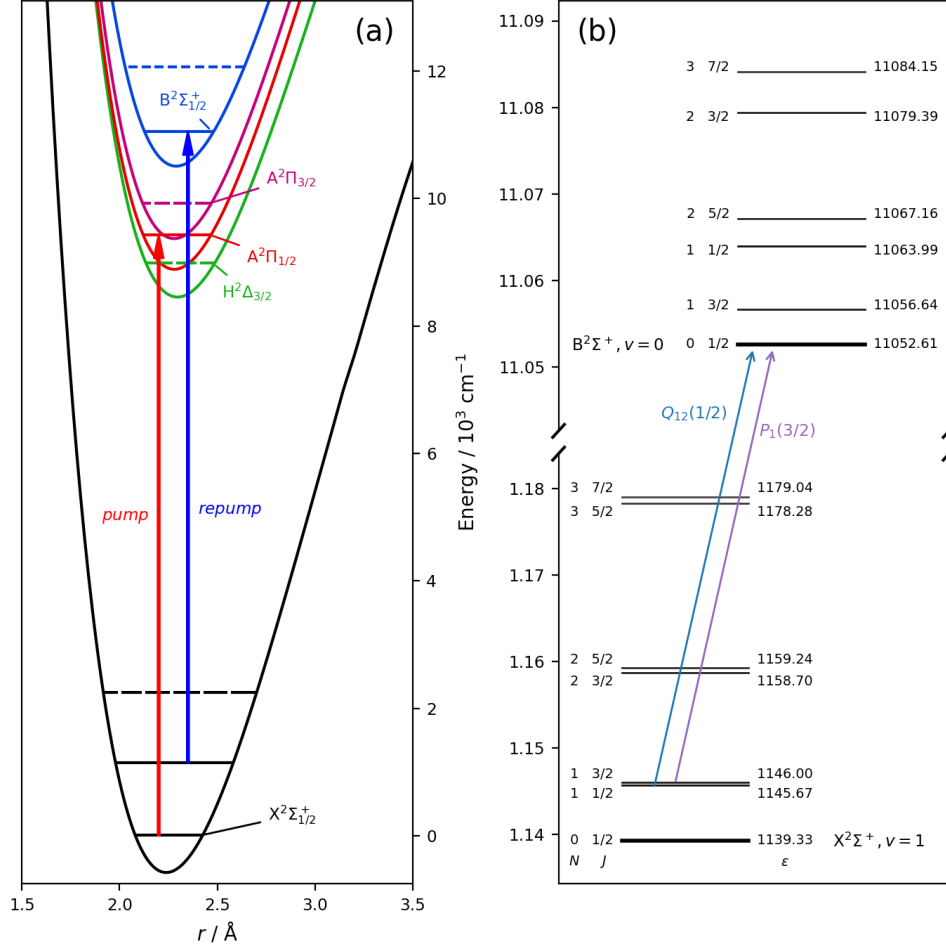


FIG. 3. (a) *Ab initio* potential energy curves of the lowest electronic states involved in laser cooling BaH. The potential energy curves and spin-orbit matrix elements are determined by the MRCI method (with Davidson correction) using MOLPRO [31] with the ACVQZ basis set on Ba and a similar basis set for H. The $H^2\Delta$ and $A^2\Pi$ potentials lie below $B^2\Sigma^+$ in the FC region. The vibrational levels directly involved in cooling are marked by solid lines, while the dashed lines correspond to the principal losses (unpumped vibrational levels), specifically the $H^2\Delta_{3/2} v=0$ (largest single decay, green), $A^2\Pi_{3/2} v=0$ (purple) and $X^2\Sigma^+_{1/2} v=2$ (black) levels. Also marked is the $B^2\Sigma^+_{1/2} v=1$ level (dotted blue line) involved in the absorption measurements reported here. (b) Calculated BaH rotational structure in the lowest $^2\Sigma^+$ states. The ACVQZ $X^2\Sigma^+$ was replaced by a more accurate MLR potential based on a Complete Basis Set (CBS) calculation [22]. The lowest rotational energies for each vibronic level are plotted. The vibrational spacings correspond to the *ab initio* values determined by DUO with the lowest vibrational level in each state anchored to experimental measurements. The zero-energy reference is the lowest rovibrational level of $X^2\Sigma^+$, 580 cm^{-1} above the potential minimum. Also marked is the $B^2\Sigma^+_{1/2} v=0, N=0 \leftarrow X^2\Sigma^+_{1/2} v=1, N=1$ repumping transition proposed for laser cooling of BaH.

theoretical value is too high, by as much as 380 cm^{-1} . As a consequence, the calculated energy difference $\Delta E = E(A^2\Pi_{1/2} - B^2\Sigma^+_{1/2})$ is in error by 20 – 25%. This has a strong effect on the value of the spin-rotation constants and must be corrected.

In general, the agreement between spectroscopic values is less satisfactory for r_e than for T_e . Where r_e is not directly quoted in a reference, it may be calculated from B_e using

$$r_e = \left(\frac{h}{8\pi^2 \mu c B_e} \right)^{1/2}, \quad (6)$$

where μ is the reduced mass in kg, c is the speed of light in cm s^{-1} , h is Planck's constant in J·s, and B_e is the rotational constant in cm^{-1} . In cases where only B_v values are quoted in the reference, B_e is extrapolated as

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \delta_e(v + \frac{1}{2})^2. \quad (7)$$

In BaH such situations typically involve only B_0 and B_1 , thus the square term is neglected and the extrapolation becomes

$$B_e = \frac{3}{2}B_0 - \frac{1}{2}B_1. \quad (8)$$

Equation (8) was used in Moore18 to determine the measured r_e values of the excited states for the selected experiments (no extrapolation was necessary for the $B^2\Sigma^+$ state).

The consensus ground-state bond length has been determined to 0.01 pm accuracy as 2.2319 Å, while the last four experiments yield 2.23188 Å within 0.005 pm. This value is used to determine $\Delta(r_e)$, the difference between the excited and ground bond lengths, for each experiment that presented r_e values for the $5d$ -complex excited states. These differences are tabulated in Table III and plotted in Figure 4. The theoretical values from Moore18 are also included for reference.

The minimum in the $B^2\Sigma_{1/2}^+$ state reported by Appelblad *et al* [11] is consistent with the earlier r_e measurements [5, 7] at the 0.1 pm level. However, it is nearly 1.9 pm shorter than the value determined by Bernard *et al* [15]. Furthermore, the earliest work on the $B^2\Sigma_{1/2}^+$ spin-rotation constant [5, 7] reports a relatively large and negative value (i.e. the level with the higher value of J lies at a lower energy) $\gamma_0 = -4.84 \text{ cm}^{-1}$ (the subscript refers to the $v = 0$ level) while Bernard *et al* [15] suggests a much smaller and positive value of $\gamma_0 = 0.46149 \text{ cm}^{-1}$, reversing the ordering of the levels. The contemporaneous value from Appelblad *et al* is more precise than the older data [5, 7] but is clearly in agreement, $\gamma_0 = -4.7538 \text{ cm}^{-1}$.

Using *ab initio* potentials without adjustment (Table II), the spin-rotation constant computed by DUO is $\gamma_0 = -5.6295 \text{ cm}^{-1}$. The $A^2\Pi$ potential was then lowered by 385 cm^{-1} to match the measured T_0 value from Ref. [9] and the spin-rotation constant recalculated (Table IV). This adjusted value $\gamma_0 = -4.9039 \text{ cm}^{-1}$ is in much better agreement with the value from Appelblad *et al* but appears to contradict the small, positive value found by Bernard *et al*.

Determining the branching ratios

The program DUO [40] was also used to determine the decay pathways and branching ratios from the *ab initio* potentials and assorted calculated matrix elements [41]. The lifetimes of each rovibronic state is calculated using the MRCI TDMs [39]. The TDMs involved in both the $A^2\Pi \rightarrow X^2\Sigma^+$ and $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions are of similar magnitude and hence the lifetimes of these two states are likely to be comparable. Also strong is the TDM connecting the $A^2\Pi$ and $H^2\Delta$ states, but $B^2\Sigma^+ \rightarrow A^2\Pi$ is considerably weaker than the other three. These minor TDMs are important because they are responsible for the main radiative loss pathways for the $A^2\Pi_{1/2} \rightarrow X^2\Sigma_{1/2}^+$ and $B^2\Sigma_{1/2}^+ \rightarrow X^2\Sigma_{1/2}^+$ cooling cycles [23]. The presence of spin-orbit mixing introduces a new and significant decay pathway $B^2\Sigma_{1/2}^+ \rightarrow H^2\Delta_{3/2}$ that competes

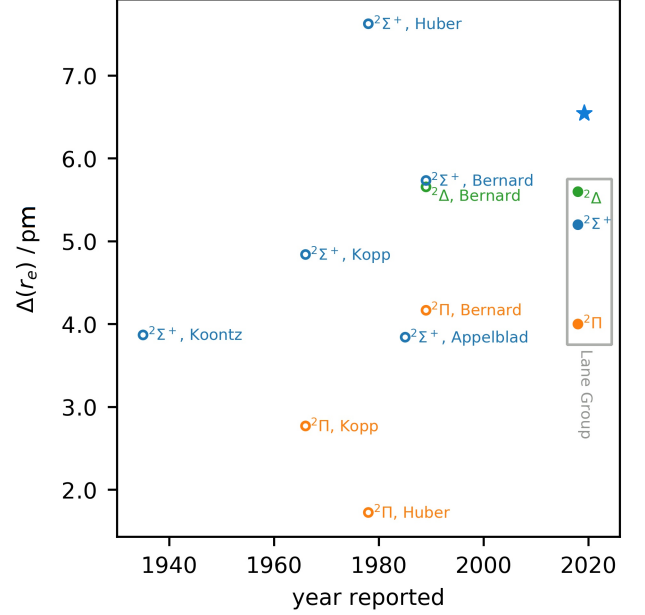


FIG. 4. A timeline for the observed values of $\Delta(r_e)$, for the lowest excited states $H^2\Delta$ (green), $A^2\Pi$ (orange) and $B^2\Sigma^+$ (blue). Also marked are the *ab initio* values of Moore and Lane [23] calculated with MRCI wavefunctions using the ACVQZ basis set. The recommended $B^2\Sigma^+$ value, based on the branching ratio measurements and the *ab initio* calculations presented here, is indicated by a star.

with the Laporte-allowed decay channels of the $B^2\Sigma_{1/2}^+$ state, as detailed in Table V.

Besides the TDM, the quantities that affect the lifetimes are the FC factors and the difference $\Delta(r_e)$ between the upper and lower states is especially important for determining these. The decay rate associated with an electronic transition can be expressed in terms of the Einstein A-coefficients for the transitions involved, defined within the DUO code [40] as

$$A_{v'v''} = \frac{16\pi^3}{3\epsilon_0 h} (2J'' + 1) \bar{\nu}_{v'v''}^3 \sum_n \left[(-1)^{\Omega''} \begin{pmatrix} J'' & 1 & J' \\ \Omega'' & n & \Omega' \end{pmatrix} \langle v' | \mu_n(r) | v'' \rangle \right]^2 \quad (9)$$

where $\langle v' | \mu_n(r) | v'' \rangle$ is the vibrationally averaged transition dipole moment, the matrix represents a $3j$ -symbol, and the summation is over all components of the transition dipole. Due to the vibrational averaging, any error in the calculated values of T_e and r_e reduce the accuracy of the calculated decay rates and the excited state lifetimes.

State	Isotope	B_e / cm^{-1}	r_e / \AA	T_e / cm^{-1}	Year	Reference
$X^2\Sigma^+$	$^{138}\text{Ba}^1\text{H}$	3.359 ^{a(3)}	2.239 ^d	(573.35)	2018	Moore and Lane [23], theoretical
	$^{138}\text{Ba}^1\text{H}$	3.38243550	2.23188651	(580.5627)	2013	Ram and Bernath [19]
	$^{138}\text{Ba}^1\text{H}$	3.3824544 ^{a(1)}	2.23188 ^c	(580.56260)	1993	Walker, Hedderich and Bernath [17]
	$^{138}\text{Ba}^1\text{H}$	3.382547 ^{a(1)}	2.23185 ^c	(569.64)	1989	Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.382477	2.2318987	(580.597)	1988	Magg, Birk and Jones [14]
	$^{138}\text{Ba}^1\text{H}$	3.382263	2.23194 ^c	(580.5673)	1985	Appelblad, Berg and Klynning [11]
	$^{138}\text{Ba}^1\text{H}$	3.38285	2.23175	(580.53)	1978	Huber and Herzberg [10]
	$^{138}\text{Ba}^1\text{H}$	3.38285	2.23175 ^c	(580.53)	1966	Kopp, Kronekvist and Guntch [9]
	$^{138}\text{Ba}^2\text{H}$	1.7072	2.2303 ^d	(413.05)	1966	Kopp and Wirhed [8]
	$^{138}\text{Ba}^1\text{H}$	3.3825 ^{a(1)}	2.2319 ^c	–	1935	Koontz and Watson [7]
$H^2\Delta$	$^{138}\text{Ba}^1\text{H}$	3.125 ^{a(3)}	2.295 ^d	9698.98	2018	Moore and Lane [23], theoretical
	$^{138}\text{Ba}^1\text{H}$	3.2174225	2.288404	9242.8	1992	Allouche <i>et al</i> [21] citing Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.217423 ^{a(1)}	2.28840 ^c	9243.13	1989	Bernard <i>et al</i> [15]
$H^2\Delta_{5/2}$	$^{138}\text{Ba}^1\text{H}$	3.14998 ^{a(1)}	2.31277 ^c	8888.644 ^{a(1)}	1987	Fabre <i>et al</i> [12]
	$^{138}\text{Ba}^1\text{H}$	2.97	–	10609	1978	Huber and Herzberg [10]
$A^2\Pi$	$^{138}\text{Ba}^1\text{H}$	3.280 ^{a(3)}	2.279 ^d	10076.45	2018	Moore and Lane [23]
	$^{138}\text{Ba}^1\text{H}$	3.3004 ^b	2.25945 ^c	9698.64	1966	Kopp, Kronekvist and Guntch [9]
	$^{138}\text{Ba}^1\text{H}$	3.25965	2.273533	9727.2	1992	Allouche <i>et al</i> [21] citing Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.25965 ^{a(1)}	2.27353 ^c	9728.67	1989	Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.300 ^b	2.249	9698.64 ^b	1978	Huber and Herzberg [10]
$B^2\Sigma^+$	$^{138}\text{Ba}^1\text{H}$	3.270 ^{a(3)}	2.291	11112.61	2018	Moore and Lane [23]
	$^{138}\text{Ba}^1\text{H}$	3.268795	2.27035 ^c	11092.5926	1985	Appelblad, Berg and Klynning [11]
	$^{138}\text{Ba}^1\text{H}$	3.21525	2.321905	10992.3	1992	Allouche <i>et al</i> [21] citing Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.215253 ^{a(1)}	2.28918 ^c	10993.31	1989	Bernard <i>et al</i> [15]
	$^{138}\text{Ba}^1\text{H}$	3.266 (3.164)	2.308	11092.44	1978	Huber and Herzberg [10] citing Veseth [43]
	$^{138}\text{Ba}^2\text{H}$	1.6355	2.2787 ^d	11089.60	1966	Kopp and Wirhed [8]
	$^{138}\text{Ba}^1\text{H}$	3.2682 ^{a(2)}	2.2706 ^c	–	1935	Koontz and Watson [7]
	$^{138}\text{Ba}^1\text{H}$	3.232 ^e	–	–	1933	Watson [5]
$E^2\Pi$	$^{138}\text{Ba}^1\text{H}$	3.522 ^a	2.190	14871.07	2018	Moore and Lane [23]
	$^{138}\text{Ba}^1\text{H}$	3.520609	2.187651	14830.1578	2013	Ram and Bernath [19]
	$^{138}\text{Ba}^1\text{H}$	3.48510 ^e	2.19877 ^e	14859.889 ^e	1987	Fabre <i>et al</i> [12]
	$^{138}\text{Ba}^1\text{H}$	3.523	2.187	14830	1978	Huber and Herzberg [10]

Values selected as reference in Moore18 [23] are in **bold font**.

Values in *italics* correspond to minor isotope data.

T_e values are relative to the corresponding $T_e(X^2\Sigma^+) = 0 \text{ cm}^{-1}$, with the zero-point energy listed in parenthesis for the X state where available.

^a Extrapolated from vibrational level values. Number in parenthesis is the highest $(v + \frac{1}{2})$ term in the power series.

^b Determined from average value of Ω states.

^c r_e determined from corresponding B_e .

^d r_e determined from a spline interpolation of the potential energy curve.

^e Only $v = 0$ measured, so the reported values refer to that vibrational level.

TABLE II. Spectroscopic T_e and r_e values for the lowest electronic states of BaH. These have been determined from tabulated rotational constants B_e or, if these are not available, by extrapolating B_v values as outlined in the text. Theoretical values from Moore18 [23] are also included.

State	$\Delta(r_e)$ / pm	Year	Reference
$\text{H}^2\Delta$	+5.6	2018	Moore and Lane [23]
	+5.655	1989	Bernard <i>et al</i> [15]
$\text{A}^2\Pi$	+4.0	2018	Moore and Lane [23]
	+4.168	1989	Bernard <i>et al</i> [15]
	+1.725	1978	Huber and Herzberg [10]
	+2.77	1966	Kopp, Kronekvist and Guntch [9]
$\text{B}^2\Sigma^+$	+5.2	2018	Moore and Lane [23]
	+9.003	1992	Allouche <i>et al</i> [21]
	+5.733	1989	Bernard <i>et al</i> [15]
	+3.841	1985	Appelblad, Berg and Klynning [11]
	+7.63	1978	Huber and Herzberg [10]
	+4.84	1966	Kopp and Wirhed [8]
	+3.87	1935	Koontz and Watson [7]

TABLE III. $\Delta(r_e)$, the difference between the equilibrium bond lengths in the excited and ground states, from a variety of spectroscopic studies. Theoretical work of Moore18 [23] determined this value by spline interpolation of MRCI+Q *ab initio* points using the ACVQZ basis set.

T_e corrections

The first correction applied to the excited states is to match the transition energies to experimental data. In Moore18, the correction to T_0 was made after analysing the *ab initio* data in DUO by replacing the calculated transition frequencies for each decay channel with the spectroscopic values from the literature. This corrects the $\tilde{\nu}_{v',v''}^3$ term in Eq. (9) for the Einstein A-coefficient.

In this work, we iteratively adjusted the energy of the potential minimum until the calculated T_0 separation was within 0.01 cm^{-1} of the spectroscopic values. To ensure the correct energetic displacement between the $\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$ states, the experimental work of Appelblad *et al* [11] was initially used as a reference for the separation between the T_0 energies in each state. Similarly, spectroscopic data from Kopp *et al* [9] was used for the $\text{A}^2\Pi$ state, and Ram and Bernath [19] for the $\text{E}^2\Pi$ state. For $\text{H}^2\Delta$, the experimental data from Bernard *et al* [15] for the spin-orbit splitting was used in combination with the spectroscopic $\text{H}^2\Delta_{5/2}$ $\nu' = 0$, $J = 5/2$ energy determined in Ref. [12]. The final energy shifts applied are -459.46 cm^{-1} ($\text{H}^2\Delta$), -385.06 cm^{-1} ($\text{A}^2\Pi$) and -99.32 cm^{-1} ($\text{B}^2\Sigma^+$). The resulting calculated spectroscopic constants are shown in Table IV. The accuracy of the *ab initio* results for the $\text{B}^2\Sigma^+$ state are particularly striking. Apart from the already discussed spin-rotation constants, the calculated values for the lowest vibrational energy separation (ΔG_{10}) in the $\text{B}^2\Sigma^+$ state (1057.16 cm^{-1}) agrees within 0.09% of the observed value (1058.04

cm^{-1}). This is a surprisingly good match to experiment for the relatively small quadruple-zeta basis set, while the performance for the other electronic states is more in-line with expectations. This change in methodology has the effect of slightly, but occasionally significantly, modifying the calculated decay rates (Table V) compared to those reported in Moore18. These rates can be expressed as raw Einstein A-coefficients for each decay channel or as the ratio of that channel to the total overall decay rate, $\mathcal{R}_{v',v''}$ in Eq. (3), a useful parameter when assessing the viability of laser cooling. No modification for a primary decay channel exceeds 0.07%, and most are $< 0.005\%$ for minor channels. However, for the $\text{B}^2\Sigma_{1/2}^+$ state there is a significant reduction in the decay to $\text{H}^2\Delta$ (from 0.054% to 0.030%) and to $v = 2$ of the ground state (from 0.014% to 0.009%). These revisions affect the fine details of the cooling efficiency (compare the “ T_0 corrected” column in Table V with Table 6 from Moore18) but do not alter the overall findings from Moore18.

r_e corrections

As $\text{B}^2\Sigma_{1/2}^+$ levels can decay to the lower $\text{A}^2\Pi$ and $\text{H}^2\Delta$ states, each with two spin-orbit components (no decay can take place to $\text{H}^2\Delta_{5/2}$), it is prudent to consider shifting the internuclear separation of these potential minima to the spectroscopic values to ensure that the calculated rates are as accurate as possible. For both components of the $\text{H}^2\Delta$ state, the only recent experimental value is from Bernard *et al* [15]. This spectroscopic $\Delta(r_e)$ is 0.055 pm different for the theoretical value, so in all simulations the $\text{H}^2\Delta_{3/2}$ potential is shifted by 0.05 pm. The equivalent shift for the $\text{A}^2\Pi_{1/2}$ state was the same as that used in the spin-rotation calculation, namely the raw *ab initio* value, as discussed below. All the tabulated theoretical values are obtained using these transformations.

The effect of adjusting r_e for the $\text{B}^2\Sigma_{1/2}^+$ potential on its lifetime is shown in Fig. 5(a). There is a smooth but significant sensitivity to Δr_e , the change in the $\text{B}^2\Sigma^+$ state r_e with respect to the *ab initio* result, even over a range of just $\pm 2 \text{ pm}$ ($\pm 0.85 \%$ of the actual bond length). A much stronger relative effect can be seen in the emission VTR [44] of Fig. 5(b),

$$\text{VTR} = \frac{q_{01}}{q_{00}} = \sum_{J''} \left(\frac{S_{0J',1J''}}{S_{0J',0J''}} \right) \quad (10)$$

where q_{0i} is the FC factor for the transition from $\text{B}^2\Sigma^+$ $v' = 0$, $J' = 1/2$ to the $\text{X}^2\Sigma^+$ $v'' = i$ vibrational level ($i = 0, 1$), and $S_{0J',iJ''}$ is the line strength factor as in Eq. (1) that is summed over the decays to both $J'' = 1/2$ and $3/2$ of $(-)$ parity. The experimental bond length shift Δr_e^{B-X} from Appelblad *et al* [11] corresponds to the dot marked A in all panels of Fig. 5. In Moore18, in an effort

State	v	T_v	A_v	B_v	$10^4 D_v$	γ_v
$X^2\Sigma^+$	0	0.00	—	3.3271	1.1359	0.2226
	1	1125.72	—	3.2622	1.1147	0.2175
	2	2227.62	—	3.1976	1.1302	0.2124
	3	3299.75	—	3.1332	1.1107	0.2073
$A^2\Pi$	0	9664.34	483.63	3.2393	1.2188	—
	1	10742.01	483.77	3.1654	1.2888	—
	2	11789.43	481.49	3.0641	-0.2486	—
	3	12809.63	488.40	3.0050	0.9440	—
$B^2\Sigma^+$	0	11052.60	—	3.2307	1.1324	-4.9039
		11052.61^a		3.2334	1.1570	-4.7539
	1	12109.76	—	3.1644	1.1261	-4.7924
		12110.64		3.1627	1.1541	-4.6343
	2	13135.59	—	3.0956	1.1401	-4.6923
		13137.94		3.0919	1.1522	-4.5178
	3	14132.49	—	3.0264	1.1650	-4.5856
		14134.65		3.0211	1.1582	-4.3897

^aUsing $X^2\Sigma^+$ zero-point energy from Appelblad *et al* [11].

TABLE IV. Vibronic state parameters as determined from the DU0 analysis of the *ab initio* results, following energy shifts to the *ab initio* MRCI+Q potentials calculated with the ACVQZ basis set on Ba. The simulation includes the lowest five electronic states ($X^2\Sigma^+$, $H^2\Delta$, $A^2\Pi$, $B^2\Sigma^+$ and $E^2\Pi$) and all the relevant spin-orbit and ladder matrix elements. These shifted potentials match spectroscopic T_0 values for each state. A_v is the spin-orbit splitting, and all values are in cm^{-1} . The $X^2\Sigma^+$ zero-point energy of 580.5673 cm^{-1} from Appelblad *et al* [11] is used for the $B^2\Sigma^+$ state. The spectroscopic values from Appelblad *et al* are shown in **bold**.

Final ro-vibronic state	(i) T_0 corrected only		(ii) Appelblad <i>et al</i>		(iii) Bernard <i>et al</i>	
	$\mathcal{A} / \text{s}^{-1}$	Ratio	$\mathcal{A} / \text{s}^{-1}$	Ratio	$\mathcal{A} / \text{s}^{-1}$	Ratio
$X^2\Sigma_{1/2}^+, v=0, N=1$	7.85×10^6	97.255%	8.05×10^6	98.553%	7.76×10^6	96.648%
$X^2\Sigma_{1/2}^+, v=1, N=1$	2.14×10^5	2.656%	1.11×10^5	1.363%	2.62×10^5	3.256%
$X^2\Sigma_{1/2}^+, v=2, N=1$	1.51×10^3	0.009%	3.51×10^2	0.004%	1.25×10^3	0.016%
$H^2\Delta_{3/2}, v=0, J=\frac{3}{2}$	2.39×10^3	0.030%	2.40×10^3	0.029%	2.40×10^3	0.030%
$A^2\Pi_{1/2}, v=0, J=\frac{1}{2}$	1.55×10^3	0.019%	1.58×10^3	0.019%	1.53×10^3	0.019%
$A^2\Pi_{1/2}, v=0, J=\frac{3}{2}$	1.33×10^3	0.016%	1.34×10^3	0.016%	1.34×10^3	0.017%
$A^2\Pi_{3/2}, v=0, J=\frac{3}{2}$	1.18×10^3	0.015%	1.20×10^3	0.015%	1.17×10^3	0.015%
Calculated VTR	0.038		0.019		0.047	
Calculated lifetime	$\tau = 123.9 \text{ ns}$		$\tau = 122.5 \text{ ns}$		$\tau = 124.3 \text{ ns}$	

TABLE V. Decay pathways from the $B^2\Sigma_{1/2}^+, v=0, N=0$ excited state of BaH. \mathcal{A} is the Einstein A-coefficient $A_{v'v''}$ for each transition, Ratio is the value of $\mathcal{R}_{v'v''}$ in percentage terms and v'' is the final vibrational level. Schemes included are (i) T_0 shifted but $\Delta(r_e)$ uncorrected from *ab initio* potentials used in Moore18 [23]. (ii) & (iii) d -complex potentials shifted to match experimental values of the $\Delta(r_e)$ value compared to the $X^2\Sigma^+$ state. (ii) uses the data of Appelblad *et al* [11] for the $B^2\Sigma^+$ state while (iii) uses the data of Bernard *et al* [15]. The calculated emission VTR is based on eqn. 10 and the calculated lifetime refers to the lowest ro-vibrational level. The recommended figures, based on the present measurements of the branching ratio, are shown in **bold**.

to minimise the effect of errors in Δr_e^{B-X} , the calculated $B^2\Sigma^+$ state is shifted to this spectroscopic value prior to determination of the decay channels. However, the agreement with the measured emission VTR of 0.092(20) is much worse than for the uncorrected potentials (third column in Table V).

To resolve this problem, the first step was to verify whether the chosen spectroscopic data is consistent with other experimental studies and *ab initio* calculations.

Comparison with the *ab initio* potentials from Moore18 (Table III) reveals a better agreement between the theoretical results and the spectroscopic Δr_e values reported by Bernard *et al* [15] for all three $5d$ -complex states, assuming that Eq.(8) is an acceptable extrapolation of the recorded B_v constants. Therefore, an additional analysis was performed by shifting all the potentials to be consistent with the measurements in Bernard *et al*. The experimental T_e is $\sim 100 \text{ cm}^{-1}$ different from Appelblad

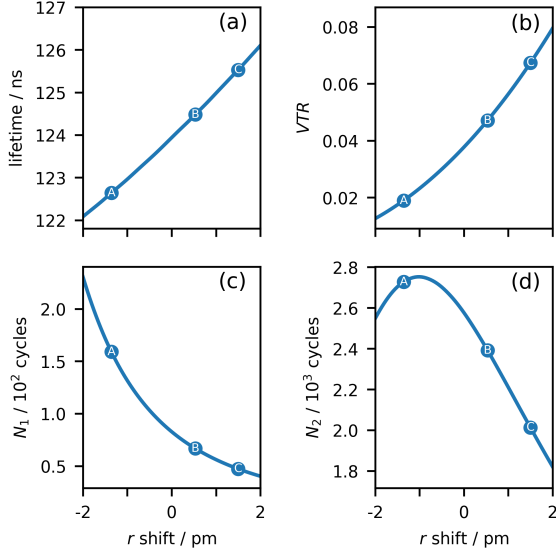


FIG. 5. Fundamental laser cooling parameters for the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition computed with MRCI wavefunctions using the ACVQZ basis set. The T_0 values have been corrected to the experimental values as described in the text. The panels present the effect of small shifts in the r_e value of the $B^2\Sigma^+_{1/2}$ state on the lifetime (a), the vibronic transition ratio (VTR, Eq. (10)) for decay to $X^2\Sigma^+_{1/2}$ $v = 1$ versus $v = 0$ (b), and the number of one-color cooling cycles N_1 (c) and two-color cooling cycles N_2 (d). The r_e shifts are relative to the *ab initio* Δr_e^{B-X} . The shifts in the *ab initio* bond length required to match the experimental difference Δr_e^{B-X} are shown with filled dots: Appelblad *et al* data [11] (A), Bernard *et al* data [15] (B), and our branching ratio data leading to the proposed longer $B^2\Sigma^+$ bond length (C).

et al used in Moore18. This small energy difference has a negligible effect on the decay rates, and this adjustment to the energy was not applied. Far more important was the Δr_e for $B^2\Sigma^+_{1/2}$. By using the Bernard *et al* value of $\Delta r_e^{B-X} = +5.733$ pm (dots marked B in Fig. 5) the agreement with the experimental branching ratio has significantly improved. The theoretical $A^2\Pi_{1/2}$ potential was a close enough match to the Bernard *et al* value of $\Delta r_e = +4.168$ pm not to warrant any shift to the *ab initio* value (Table V). The new simulation is a superior match to experiments: in particular, the calculated lifetime of the $B^2\Sigma^+_{1/2}$ state is now 124.3 ns, in excellent agreement with the lifetime of the $J = 11/2$ level measured in Ref. [18] and an improvement on the uncorrected potentials. The shift in r_e significantly increases the decay to $X^2\Sigma^+_{1/2}$ $v = 2$, to an extent that it becomes comparable to radiative decay to $A^2\Pi_{1/2}$ $v = 0$, $J = 3/2$ but is still below the decay to $H^2\Delta_{3/2}$.

Replacing the ground state potential

In addition to Δr_e , the shape of the potential energy function $V(r)$ affects the accuracy of the vibronic transition moments through changes to the vibrational wavefunction. The presently calculated aug-cc-pCVQZ $V(r)$ for $B^2\Sigma^+_{1/2}$ is of a very high quality for a quadruple-zeta potential. Describing the barium atomic orbitals using the aug-cc-pCVnZ basis sets ($n = Q, 5$) taken to the CBS (Complete Basis Set) limit [22] produces a high-quality ground state potential $X^2\Sigma^+$. The calculated r_e , for example, lies within 0.03 pm of the experimental value of Ram and Bernath [19]. Furthermore, by fitting this potential to spectroscopic data using DPotFit [45], including the correct dispersion behavior of the potential at extended bond lengths [46], a very accurate potential can be generated from the short range to the atomic threshold. The *ab initio* points were first fitted to a 13-parameter MLR potential [47, 48] using betaFIT (version 2.1) [49] and then combined with $X^2\Sigma^+$ infrared experiments [17] and $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission data [5, 7, 8] for processing with DPotFit. No measurements from Bernard *et al* [15] were used in this fitting process. As the data set contains both BaH and BaD spectroscopic information, the isotopic Born-Oppenheimer breakdown corrections [50] could also be determined. The final ro-vibrational levels for the lowest three vibrational quantum states can be reproduced with an accuracy better than 0.005 cm^{-1} . Replacing the present ACVQZ ground state with the MLR potential from Ref. [22] should improve the accuracy of the calculated transitions.

The absorption data consists of VTR measurements to the $B^2\Sigma^+$ $v = 0$ and $v = 1$ levels from $v = 0$ or $v = 1$ in the ground $X^2\Sigma^+$ state. Specifically, the $N' = 0$ $J' = \frac{1}{2}$ (+) \leftarrow $N'' = 1$ $J'' = \frac{1}{2}$ (−) absorption lines (Q_{12}) were measured for each vibrational band, $q_{v',v''}$ determined for each transition and the ratios q_{10}/q_{00} and q_{01}/q_{11} found (Table I). These experimental FC factors can be compared directly with the theoretical $S_{v',v''}$ (Q_{12} lines only so the reference to J can be dropped) line strength factors. The theoretical branching ratios can be plotted as a function of the deviation in Δr_e^{B-X} from the *ab initio* value (5.2 pm) as in Fig. 5 and then compared with measured values as shown in Fig. 6. The plot clearly demonstrates the highly sensitive dependence of q_{01}/q_{11} in particular on the bond length and that two experimental Δr_e^{B-X} values [11, 15] (dots marked A and B in Fig. 6) predict ratios that are lower than observed. We find that any discrepancies between the calculated and experimental branching ratios can be resolved by shifting the potential minimum of the $B^2\Sigma^+$ state to a longer bond length. To match experiment within error bars, a bond length difference $\Delta r_e^{B-X} = 6.5 - 7.0$ pm is necessary, requiring a $B^2\Sigma^+_{1/2}$ state bond length 0.8 - 1.3 pm greater than reported by Bernard *et al* but still somewhat

shorter (see Fig. 4) than the values reported in Huber and Herzberg [10] ($\Delta r_e^{B-X} = 7.6$ pm) and Allouche *et al* [21] (9.0 pm).

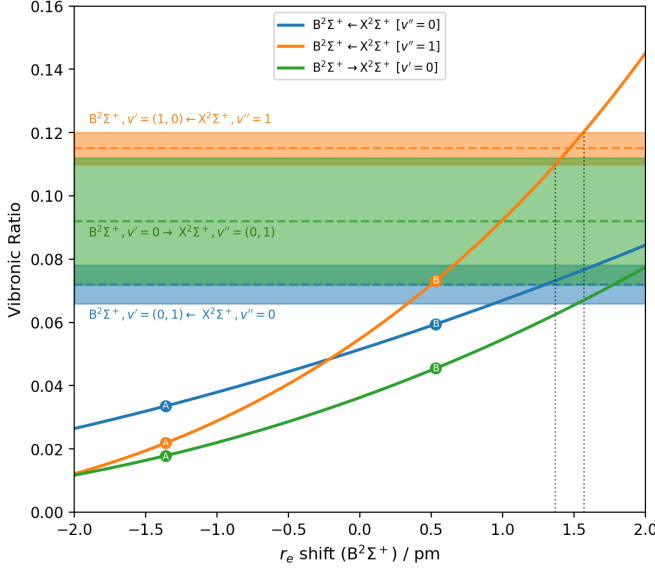


FIG. 6. Comparison between our $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ VTR (vibronic transition ratio) measurements (horizontal dashed lines, with uncertainties represented by the horizontal bars) and the predicted ratios based on *ab initio* results (solid lines). The ground state is the MLR potential based on ACVnZ/CBS MLR calculations from Ref. [22] and the excited state is based on a ACVQZ potential. The difference in equilibrium bond lengths between the two states is varied between -2 pm and $+2$ pm from the *ab initio* result $\Delta r_e^{B-X} = 5.2$ pm. The blue data (lowest horizontal bar) corresponds to q_{10}/q_{00} and the orange (highest horizontal bar) to q_{01}/q_{11} . The green data corresponds to the q_{01}/q_{00} . Also marked are the shifts in the *ab initio* bond length required to match the experimental difference Δr_e^{B-X} between the upper state value of Appelblad *et al* [11] (dots A) while the dots B are set at the value of Bernard *et al* [15]. The black dotted vertical lines represents the range of bond length corrections where the calculated and measured VTRs agree for all three experimental bands.

In addition, the q_{10}/q_{00} branching ratio was measured for the $A^2\Pi_{3/2} \leftarrow X^2\Sigma^+$ transition via absorption. When computing this VTR, the $A^2\Pi_{3/2}$ *ab initio* ACVQZ potential without r_e adjustment (as it is almost identical to Bernard *et al*) is used to simulate the measurement. The calculated q_{10}/q_{00} ratio is in excellent agreement with the experimental result (Table I).

The superior modeling of the branching ratio data using the Bernard *et al* [15] $B^2\Sigma^+$ bond length compared to Appelblad *et al* [11] indicates that to ensure an improvement in the simulation of the cooling process by correcting for experimental data, the Bernard *et al* value should be adopted over Appelblad *et al*. The decay rates were computed for the lowest rovibrational levels in all three $5d$ -complex states. The updated branching ratios confirm the conclusion of Moore18 that the $A^2\Pi \leftarrow X^2\Sigma^+$

	Decay pathways			
	Final state	v''	$\mathcal{A} / \text{s}^{-1}$	Ratio / %
$B^2\Sigma_{1/2}^+$ $v' = 0$	$X^2\Sigma_{1/2}^+ (N = 1)$	0	7.79×10^6	96.766
	$Q_{1/2}$		4.25×10^6	52.865
	P_1		3.53×10^6	43.901
	$X^2\Sigma_{1/2}^+$	1	2.52×10^5	3.131
	$Q_{1/2}$		1.90×10^5	2.359
	P_1		6.20×10^4	0.771
	$X^2\Sigma_{1/2}^+$	2	1.73×10^3	0.021
	$H^2\Delta_{3/2} (J = \frac{3}{2})$	0	2.39×10^3	0.030
	$A^2\Pi_{1/2} (J = \frac{1}{2})$	0	1.53×10^3	0.019
	$A^2\Pi_{1/2} (J = \frac{3}{2})$	0	1.35×10^3	0.017
	$A^2\Pi_{3/2} (J = \frac{3}{2})$	0	1.17×10^3	0.015
	Lifetime (ns)			124.3
$A^2\Pi_{1/2}$ $v' = 0$	$X^2\Sigma_{1/2}^+ (N = 1)$	0	7.23×10^6	98.772
	$X^2\Sigma_{1/2}^+$	1	8.94×10^4	1.221
	$X^2\Sigma_{1/2}^+$	2	1.50×10^2	0.002
	$H^2\Delta_{3/2} (J = \frac{3}{2})$	0	3.24×10^2	0.004
	Lifetime (ns)			136.5
$B^2\Sigma_{1/2}^+$ $v' = 1$	$X^2\Sigma_{1/2}^+ (N = 1)$	0	6.848×10^5	8.82
	$X^2\Sigma_{1/2}^+$	1	6.58×10^6	84.907
	$X^2\Sigma_{1/2}^+$	2	1.21×10^5	6.115
	$X^2\Sigma_{1/2}^+$	3	5.12×10^3	0.066
	$H^2\Delta_{3/2} (J = \frac{3}{2})$	1	2.26×10^3	0.029
	$A^2\Pi_{1/2} (J = \frac{1}{2})$	1	2.68×10^3	0.034
	$A^2\Pi_{3/2} (J = \frac{3}{2})$	1	2.76×10^2	0.014
	Lifetime (ns)			128.9

TABLE VI. Radiative decay pathways from the $B^2\Sigma^+ v' = 0$, $A^2\Pi_{1/2} v' = 0$, and $B^2\Sigma^+ v' = 1$ levels of BaH. \mathcal{A} is the Einstein A-coefficient for each transition and Ratio is the value of $\mathcal{R}_{v',v''}$. The excited states are represented by the ACVQZ potentials from Moore18, and Δr_e is set at the experimental value derived from Bernard *et al* [15]. The ground state is the ACVnZ/CBS MLR potential of Ref. [22]. The decay from $B^2\Sigma^+ v' = 0$ to $X^2\Sigma^+ v'' = 0$ and 1 is further decomposed into the Q_{12} and P_1 sub-branches.

transition is advantageous for Doppler cooling despite the longer wavelength of the transition, as shown in Table VI. Using two laser fields, over 99.99% of the population loss can be recycled into the cooling process. Crucially, the $A^2\Pi - X^2\Sigma^+$ cooling has a single loss channel involving another electronic state ($H^2\Delta$) while the $B^2\Sigma^+ - X^2\Sigma^+$ transition has four decay routes, all significantly stronger (Table VI).

The molecular parameters relevant to Doppler cooling are collected in Table VII. The lifetime of $H^2\Delta_{3/2}$ is determined by spin-orbit mixing with the $A^2\Pi$ state and the strength of the $A^2\Pi - X^2\Sigma^+$ TDM. The former is significantly reduced over the original calculation in Moore18, so the lifetime of the $H^2\Delta_{3/2}$ state has almost doubled to $9.5 \mu\text{s}$. The other lifetimes are nearly unchanged, although the $B^2\Sigma_{1/2}^+$ lifetime is now in even

better agreement with experiment.

The maximum number of cycles N_n that n light fields can support and maintain fraction \mathcal{F} of the molecules in the cooling cycle depends on the branching ratios $\mathcal{R}_{v'v''}$ [2, 23]. Setting \mathcal{F} to 0.1 (90% loss in molecular beam intensity), the number of cooling cycles supported by each transition can be determined for one-, two- and three-color cooling (the third transition involves excitation out of the $\text{H}^2\Delta_{3/2}$ state [23]). The change in Δr_e has had a particularly large effect on the number of one-color cooling cycles that can be supported on the A – X and B – X (Fig. 5(c)) cooling transitions. In both cases, this number has been profoundly lowered. However, using a second laser to repump $v'' = 1$ creates a nearly closed cycle (Fig. 5(d)), in particular for $\text{A}^2\Pi \leftarrow \text{X}^2\Sigma^+$ transition.

$\text{B}^2\Sigma^+$ can decay to the same lower lying $\text{H}^2\Delta_{3/2}$ as the $\text{A}^2\Pi_{1/2}$ state but additionally to $\text{A}^2\Pi_{3/2}$ and $\text{A}^2\Pi_{1/2}$ and this broader range of emission options ultimately means that it is rather more lossy than cooling on the A – X cycle. Shifting the bond length in $\text{A}^2\Pi_{1/2}$ from the experimental value of Kopp *et al.* [9] to Bernard *et al.* [15] does have a somewhat detrimental effect on the efficiency of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ cooling cycle. It is still very effective, but the number of cycles possible with two cooling lasers $N_2 = 3.53 \times 10^4$ is rather smaller than reported in Moore18 [23]. Naturally, the increased B state r_e also reduces the value of N_2 (2.25×10^3) from the previous calculation, but the relative reduction is somewhat smaller. This partly because the increased $\text{B}^2\Sigma^+$ bond length does indeed raise the decay to $\text{X}^2\Sigma^+ v'' = 2$ but this is ameliorated by the reduced decay to $\text{H}^2\Delta_{3/2}$ (the largest decay channel) the present revised calculations predict. However, using a third laser to repump the $\text{B}^2\Sigma^+_{1/2} - \text{X}^2\Sigma^+_{1/2}$ cooling cycle will only have a marginal improvement on the efficiency ($N_3 = 3.17 \times 10^3$) while it more than triples the corresponding number of $\text{A}^2\Pi - \text{X}^2\Sigma^+$ cycles.

Using the superior ground state potential does not improve the agreement between the calculated and measured emission VTR q_{01}/q_{00} (last line in Table I), lowering the theoretical $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$ value to 0.045 compared with 0.047 with the ground ACVQZ potential (Table V). Any remaining discrepancies between the calculated and experimental branching ratios can be resolved by shifting the potential minimum of the $\text{B}^2\Sigma^+$ state to a longer bond length as with the absorption data. The arithmetic mean for the bond increase determined from the absorption and emission data is +1.5(1) pm.

The poorer agreement observed in the B – X emission calculations is removed when only the ratio of Q_{12} lines are compared (as in the absorption simulations). Adopting the adjustment to the Bernard *et al* [15] Δr_e^{B-X} , the ratio of emission linestrengths S_{01}/S_{00} is 0.062 for the Q_{12} lines while this falls to 0.024 for the P_1 lines (Table VI). The former value is in very good agreement with experiment and with the calculated FC factors (Table

Molecular data	States		
	$\text{B}^2\Sigma^+_{1/2}$	$\text{A}^2\Pi_{1/2}$	$\text{H}^2\Delta_{3/2}$
λ/nm	905.3	1060.8	1110
τ/ns^a	124.3 (125.7)	136.5	9532
N_1	70 (47)	186	-
$N_2 (\times 10^3)$	2.3 (2.0)	35.3	-
$N_3 (\times 10^3)$	3.2 (3.0)	122	-
$T_D/\mu\text{K}$	30.7 (30.3)	27.9	0.4
$v_c/\text{cm s}^{-1}$	116.1 (114.8)	123.8	1.8
$v_D/\text{cm s}^{-1}$	4.3 (4.2)	4.1	0.5
$a_{\text{max}}/\text{ms}^{-2}$	$12.7(12.6) \times 10^3$	9.9×10^3	-

^a For the lowest rovibronic level.

TABLE VII. Revised calculated properties of the proposed laser cooling transitions in BaH molecules. The differences in equilibrium bond lengths, Δr_e , are set at the experimental values from Bernard *et al* [15] (the *italicised* values correspond to the longer excited bond length proposed here). Here N_i is the number of cycles supported by i lasers before the population falls to 10%, T_D and v_D are the Doppler temperature and velocities, v_c is the capture velocity, and the maximum deceleration is $a_{\text{max}} = \frac{\hbar k \gamma}{2M} = v_r \frac{A}{2}$.

Adjustment	$\text{B}^2\Sigma^+_{1/2} - \text{X}^2\Sigma^+_{1/2}$ FC factors			
	(00)	(01)	(02) $\times 10^3$	(03) $\times 10^6$
Bernard Δr_e^{B-X}	0.937	0.062	0.65	1.4
+ 1.5(1) pm	0.922(4)	0.077(4)	1.09(9)	2.5(2)

TABLE VIII. Effect of adjusting the *ab initio* $\text{B}^2\Sigma^+$ and $\text{X}^2\Sigma^+$ potentials on laser cooling. The FC factors are calculated using the program DUO [40]. The top row corresponds to the excited $\text{B}^2\Sigma^+_{1/2}$ state represented by the ACVQZ potentials from Moore18. The excited-ground state bond length difference Δr_e is set at the experimental values derived from the experiments by Bernard *et al* [15]. The ground state used is the ACVnZ/CBS MLR potential of Ref. [22]. The bottom row adds a further extension to the excited state bond length so that it differs by + 1.5(1) pm from the *ab initio* result.

VIII), perhaps indicating that the the calculated P_1 line for the $v' = 0 - v'' = 1$ transition is too weak.

The principal effect of a longer excited-state bond length ($\Delta r_e^{B-X} = 6.7$ pm) on the cooling is to increase the loss to $v'' = 2$ and thus reduce the efficiency. These changes can be quantified by comparing the FC factors at the Bernard *et al* bond length with the longer value proposed here, as shown in Table VIII. There is almost a 70% increase in the decay to $v'' = 2$. The improved agreement with the VTR measurements is presented in Table I. The associated slight increase in excited state lifetime (still in excellent agreement with experiment) and reduction in the length of the $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$ cooling cycles (N_n) are documented in both Fig. 5 (dots C) and Table VII.

Repumping both $v = 0$ and $v = 1$ levels in the $\text{X}^2\Sigma^+$

state via the lowest vibronic level of the $A^2\Pi_{1/2}$ state is the preferred option to keep radiative losses to a minimum. Practically, to take advantage of maximum radiation pressure forces, implementations of laser cooling often avoid transitions that share the same excited level. Unfortunately, pumping the $v' = 1$ level in the $A^2\Pi_{1/2}$ (or $B^2\Sigma_{1/2}^+$) state will significantly increase the decay rate to $v'' = 2$ and will even open decay to $v'' = 3$ [23]. Consequently, a combination of transitions involving $A^2\Pi - X^2\Sigma^+ (0 - 0)$ and $B^2\Sigma^+ - X^2\Sigma^+ (0 - 1)$ is the best compromise cooling scheme by virtue of having the lowest additional losses (approximately 0.0015% losses per cycle), although the increased excited-state loss from $B^2\Sigma_{1/2}^+$ means that the two-color efficiency is reduced to $N_2 = 2.84 \times 10^4$ cycles.

One additional loss channel to consider is possible vibrational decay via infrared emission within the $X^2\Sigma^+$ ground state, particularly from the $v = 1, N = 1$ level as it participates in the two-color cooling cycle. The relatively large vibrational spacing of hydrides could result in a significant Einstein A-coefficient over rival ultracold diatomic molecules such as fluorides, oxides, or alkali metal dimers. The upper $J' = 3/2 (-)$ level can decay via three radiative transitions while there are two pathways for the lower $J' = 1/2$. In both cases, the decay to $N'' = 2, J'' > J'$ leads to the largest loss rate. The total decay rates for $J' = 3/2$ and $J' = 1/2$ are 79.2 s^{-1} and 79.3 s^{-1} , respectively, resulting in practically identical radiative lifetimes of 12.6 ms. This vibrational loss can be mitigated by operating the repumping lasers well above saturation and thus ensuring that the molecules spend minimal time in the $X^2\Sigma^+ v = 1$ state. This radiative pathway could also allow us to populate the absolute ground rovibronic state $v = 0, J = 1/2 (+)$ after cooling by pumping into $v = 1$, loading the molecules into a conservative trap, and waiting a short time for them to decay. This is a unique feature of diatomic hydrides (as compared to other laser cooling candidates) due to their larger vibrational spacing.

CONCLUSIONS

The branching ratios of diagonal molecular transitions are extremely sensitive to the relative bond lengths between the excited and ground states. In this work, the vibrational branching ratios for the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition in BaH molecules was measured via optical fluorescence and absorption, and calculated using *ab initio* quantum chemistry methods. By shifting the excited-state potential by just 0.5 pm (0.25% of the bond length), an improved agreement with former experiments is achieved, particularly with spectroscopic r_e values for the excited states from Bernard *et al* [15]. Furthermore, our measured branching ratio indicates that the *ab ini-*

tio excited-state $B^2\Sigma^+$ potential should be shifted by +1.5(1)pm relative to the ground state. This bond length correction is found to have implications for the closure of the $B^2\Sigma^+$ state with respect to laser cooling, confirming the $A^2\Pi_{1/2}$ excited state as a superior choice. The sensitivity of branching ratios to small changes in Δr_e , and the substantial inconsistency in the estimates of this parameter present in the literature, show that care must be taken when identifying potential laser cooling candidates.

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